

Inedible Fats and Fatty Acids. History and Technological Trends

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860

FOR many years inedible fats and oils played a role in our economy characterized by the development of few significant technical changes and trends. Around the turn of the century there was considerable technical and scientific interest in fats and



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oils connected chiefly with their use as candle materials, lubricants, and textile processing adjuvants. The extent of this interest was expressed by the publication and frequent revision of the three-volume work by Lewkowitsch (10). The period was culminated by the development of workable processes for separating liquid and solid glycerides and more significantly for separating "stearic" and "oleic" acids; the separation of these acids followed the batchwise catalytic hydrolysis of the parent glycerides. These separations in both cases involved removal

of the higher melting crystalline components from the lower melting liquid fraction; the actual separation was made by filtration under pressure. Distillation of the fatty acids was also practiced commercially.

Following this period, competition of petroleum illuminants and lubricants combined with the development of a ready outlet for fats in the growing soap industry to furnish little incentive for research and development in the field of fats and fatty acids. Hence it is not surprising that the period for several decades up to about 1935 was characterized by few basic changes in the processing of inedible fats and fatty acids. This, of course, also resulted in the fact that relatively few new products derived from inedible fats were marketed and that their field of utilization remained static by comparison with the simultaneous development taking place in other branches of the chemical industry.

It should not be inferred from this that no progress was made in fat and fatty acid handling and utilization during the period, but rather that the progress which took place was largely limited to improvements of existing processes and to such improvement of the products as could be achieved by mixing and blending.

In retrospect it is apparent that during the '30's a number of technical leaders concluded that inedible fats and oils could not continue their rightful place in our economy without the development of improved processes for commercially achieving better separations. One underlying reason for this thinking has been enunciated very clearly by Potts (12), who pointed out that the use of natural oils has frequently forced manufacturers to use varying amounts of fatty

acids that are not only of no value for the specific purpose but in some cases are even detrimental to the final product. It will be realized that this same statement can be applied equally well to mixed fatty acids of the type then generally available, and numerous examples of this truth may be cited. Basically two reasons may exist for removing those components of a fat or fatty acid mixture which are undesirable for a specific use. One the one hand, their removal may be necessary to meet competition on a quality basis while, on the other hand, their removal may be economically advantageous.

Because of the mixed character of the glycerides it was logical for the principal effort to be directed first to separation of the fatty acids. Two basic methods for fractional separation of fatty acids appeared to hold promise for commercial use. These, of course, were fractional distillation and fractional crystallization from solvents, each of which offers certain advantages and disadvantages.

Of these two processes fractional distillation was the first to be practiced on a commercial scale. The first fractional distillation unit based on the patent of Potts and McKee (13) went into operation in 1933 and was expanded by installation of a second unit in 1941 (8). Commercial fractional distillation has permitted the production and marketing of relatively pure (ca. 90%) members of the series of saturated fatty acids since separation could be made based on the number of carbon atoms in the chain. It has not permitted separation of the unsaturated fatty acids from those saturated acids having the same number of carbon atoms. Thus, for example, palmitic and stearic acids are readily separable by fractional distillation, but oleic and stearic acids are not.

In this respect the fractional crystallization of fatty acids serves to complement their fractional distillation very well. Considerable information regarding separation and purification of fatty acids by low temperature crystallization was available by 1941. The principal investigator in this country was J. B. Brown (2).

The first fractional crystallization unit for purification of fatty acids on a commercial scale went into operation in 1942 (9). Published information (3) indicates that solvent fractional crystallization has found its principal use in the separation of the saturated acids from the more soluble unsaturated ones. It is probable that the process also offers advantages over the previously used graining and pressing operation for separating saturated acids differing in molecular weight, for separating unsaturated acids differing in unsaturation and for separating glycerides by virtue of differences in unsaturation.

In some cases a combination of steps can be used to attain an end which is otherwise unattainable. The first process proposed for the commercial preparation of a purified monoethenoic acid (oleic) is an example of such a combination (15). The desired results were obtained by alteration of the polyunsaturated acids in tallow or grease by hydrogenation, followed by sep-

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aration of the saturated acids either by crystallization or pressing methods. The unsaturated acids resulting from such treatment are essentially monoethenoic in nature. A modification of this approach to the preparation of commercially pure oleic acid has been described by Goebel (5). This worker reduced the content of polyunsaturated components to very low levels by their selective polymerization in the presence of steam, which serves to minimize decarboxylation.

Improvements in low temperature crystallization processes now make it commercially practicable to prepare a purified grade of oleic acid directly from stocks containing other unsaturated acids. It is advantageous in the use of this process to prepare oleic acid and to combine it with a selection of raw material containing relatively low proportions of polyunsaturates.

Another process offering theoretical possibilities for use in preparing pure fatty acids and monoesters is liquid-liquid extraction. Although considerable work in this field has been reported, commercial application of the technique seems to have been confined largely to operations upon glycerides. Still another process for purifying fatty acids, the practical possibilities of which may not yet be fully realized, is based on the use of urea complex formation.

A unique solvent method for purifying the solid saturated acids has been described by Jenness (7) In this process the subdivided solid acids are washed with a solvent which removes unsaturated acids and other soluble impurities. The process is used commercially to prepare stearic acid of about 97% purity.

Turning now to the oils themselves, we find that the early literature in fat chemistry records many painstaking attempts to isolate pure triglycerides from fats even though Berthelot (1) pointed out 100 years ago that they were probably composed of mixed triglycerides rather than mixtures of simple triglycerides. As a result of considerable research in the field, chiefly by Hilditch and co-workers, we now understand why these endeavors were so fruitless despite the undoubted skill of those early investigators in carrying out fractional crystallizations. Because of the random or nearly random distribution of the fatty acids in most cases, the natural fats are extremely complex and pure simple triglycerides are not present in more than small percentages unless the fat contains one fatty acid to the extent of more than 67%, a condition found in very few natural fats.

Nevertheless solvent extraction processes have been used to separate semi-drying oils, such as soybean oil, into drying and non-drying fractions on a commercial basis (4). They have also been used to segregate nonglyceride materials in natural fats into fractions. Most notably in this respect they have been used to segregate a vitamin fraction from fish oils and to "upgrade" tallow by segregation and removal of color bodies and other impurities (11). Although a wide variety of solvents have been proposed, only two appear to have been used to any extent commercially. They are furfural (4) and propane (11).

Some separation of glycerides can also be achieved by the use of molecular distillation techniques. Because of the limitations of fractionation obtainable and the extremely heterogeneous character of most natural fats, this process has generally found its use confined to segregation of nontriglyceride materials present in fats. For example, it may be used to con-

centrate and isolate vitamins, monoglycerides, and the like.

Summarizing separation processes, it is obvious that if industrial needs can be satisfied by the segregation of a selected group of triglycerides from an oil, such segregation can undoubtedly be achieved more economically by application of one of the above processes to the oil, rather than by splitting the fat, purifying the fatty acids, and resynthesis of the glycerides. On the other hand, it is well to keep in mind other factors before coming to a final decision regarding the relative merits of the several processes usually available for achieving desired results. For example, solvent segregation of glycerides has usually been proposed for use in fractionating an oil or fat so that a portion of it could compete with an oil or fat more favorably situated economically because of its different chemical constitution. The economic premiums for oils having specific properties are tending to disappear however, because of increasing scientific knowledge which is leading to increasing interchangeability among fats and oils. Moreover, when a segregated product is to be used in competition with synthetic products on a quality basis, it may be required to have properties which will prove difficult to attain by a relatively simple operation from mixed triglycerides.

The chief reason for the development of processes for commercially preparing fatty acids and glycerides of greater chemical homogeneity is in order to find outlets in the chemical industry. It is therefore well to turn for a moment to the consideration of trends in this area.

Fatty acids as such can undergo two basic types of reaction. These are carboxyl modification and chain modification which can be used to produce important products shown below. In some cases the significance of these compounds lies chiefly in their value for use as intermediates for further synthesis.

I. PRODUCTS OBTAINED BY CARBOXYL GROUP REACTIONS

- a) Acid halides
- b) Salts — organic and inorganic
- c) Nitrogen derivatives
 - Nitriles — amides — amines — quaternaries
- d) Alcohols, aldehydes, and hydrocarbons
- e) Esters
 - Monohydric, polyhydric, polyoxyethylene, polymerizable

II. PRODUCTS OBTAINED BY CHAIN MODIFICATION

From Saturated Acids

- a) Substitution
 - Halogenated Products
 - α -Sulfonates

From Unsaturated Acids

- b) Addition
 - Hydrogenated Products
 - Halogenated Products
 - Hydroxylated Products — mono- and di-
 - Oxidation Products — peracids, epoxides, etc.
 - Ozonolysis — to cleavage products
 - Sulfurization, Sulfation and Sulfonation
 - Nitrogen Derivatives
 - Aromatics
 - Polymers, homo and hetero
 - Diels-Alder type Adducts
- c) Isomerization
 - Isomers obtained by:
 - Elaidinization
 - Double Bond Shift

On the other hand, a number of the derivatives listed find their principal outlets as such. Among these might be listed such important ones as the salts, esters such as monoglycerides, which have their principal use as emulsifiers in shortening and margarine,

and the epoxides which are used as plasticizing stabilizers.

Not all of these products have practical value in the usual sense, but many of them do; and the remaining ones have practical significance in that they are promising intermediates. Quite a few of the more important ones, notably epoxides and polymerizable esters, such as the vinyl esters, have been added to the list in the last decade although not always in the sense that they are entirely novel compounds. In some instances their inclusion in the list indicates that commercial methods have been developed for preparing compounds which only a few years ago were in the class of laboratory curiosities. It is to be expected that further additions to the list will occur at an accelerated rate as a result of increasing research.

It will be noted, of course, that all of the reactions can be performed upon unsaturated acids while the saturated acids only lend themselves to carboxyl modification and chain substitution or isomerization reactions. In the hands of a research chemist the unsaturated fatty acids are more mutable and over the long term will therefore probably tend to be more valuable. It should also be kept in mind that satisfactory commercial processes are available for converting unsaturated fatty compounds to the corresponding saturated ones but that the reverse is not feasible on a commercial scale.

The development of satisfactory household detergents has stimulated the search for new uses for fatty acids in the chemical field. The economic pressures resulting from increasing production of tall oil fatty acids, a by-product of paper manufacturing, coupled with the growing amounts of animal fats available from the expanded livestock industry have accelerated the pace of this search.

It is hardly possible, as yet, to foresee what effect the recent and rapidly growing use of inedible animal fats in animal feeds may have upon their consideration for such other purposes as chemical raw materials. At present however it appears probable that decreasing consumption of fats in soap production both in the United States and abroad will combine with an increased production of inedible fats of several types to assure continued availability of fats for chemical conversion. It is well to remember that the extremely low prices for fats which have characterized the past several years were symptomatic of a "sick" industry, which was to be regarded as a poor base for extensive development.

It would not be proper to conclude this paper without referring to the paramount importance of continued and further development of improved analytical methods. Such methods are the tools essential to the research chemist in his efforts to develop the constant stream of new products which our competitive world requires; they are also essential to the production man for controlling the quality of the products being made and used in the fat industry.

The relatively recent development of the ultraviolet spectrophotometric method for precise study and determination of the unsaturated acids has been a great step forward, particularly the development of a micro method (6). The use of the infrared spectrophotometer has also been found of great value for the study of *cis*- and *trans*-isomers (14).

At present however anything like a precise determination of fatty acid constitution according to chain length still calls for a quantitative fractional distillation which requires considerable time. Some recent work using chromatographic methods indicates a possible way out of this dilemma.

Improved methods are urgently needed for study of glyceride composition, fatty acid composition according to chain length, and for fatty acid reaction products, such as those produced by many chemical reactions and biochemical processes.

In conclusion, it may be stated that our brief and limited examination of the history of the inedible fat and fatty acid industry shows the existence of a number of trends. Undoubtedly a considerable proportion of these will persist into the future. First, and probably most significant, is the ever-increasing role which research is playing in the maintenance of old uses and the development of new ones. An example of the former is the role played by research in maintenance of the use of fatty acid soaps as emulsifiers in the manufacture of synthetic rubber. Research has even come to be essential in developing uses for fats in which no substantial modification of the fat is required. An outstanding illustration of this is the recent development of the use for inedible fats in animal feeds. This use was dependent upon the development of satisfactory antioxidants for stabilizing the fats and also upon subsequent nutritional research.

Somewhat as a result of the increasing impact of research it can be expected that increasing attention will be given to the manufacture of products with increasing chemical homogeneity, *i.e.*, more nearly pure compounds. At any rate it will be necessary to know more about the nature of any impurities present in the materials. This will be essential in order to profitably produce competitive products. This industry should realize that customers will not continue indefinitely to buy a product which is contaminated with an unwanted and undesirable component.

Indications are that the development of diversified markets will tend to lead fatty acid producers and processors into a much greater variety of manufacturing and processing operations. In fact, it seems probable that the industry as a whole will largely assume the characteristics and become a segment of the chemical industry.

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